PB81-226185

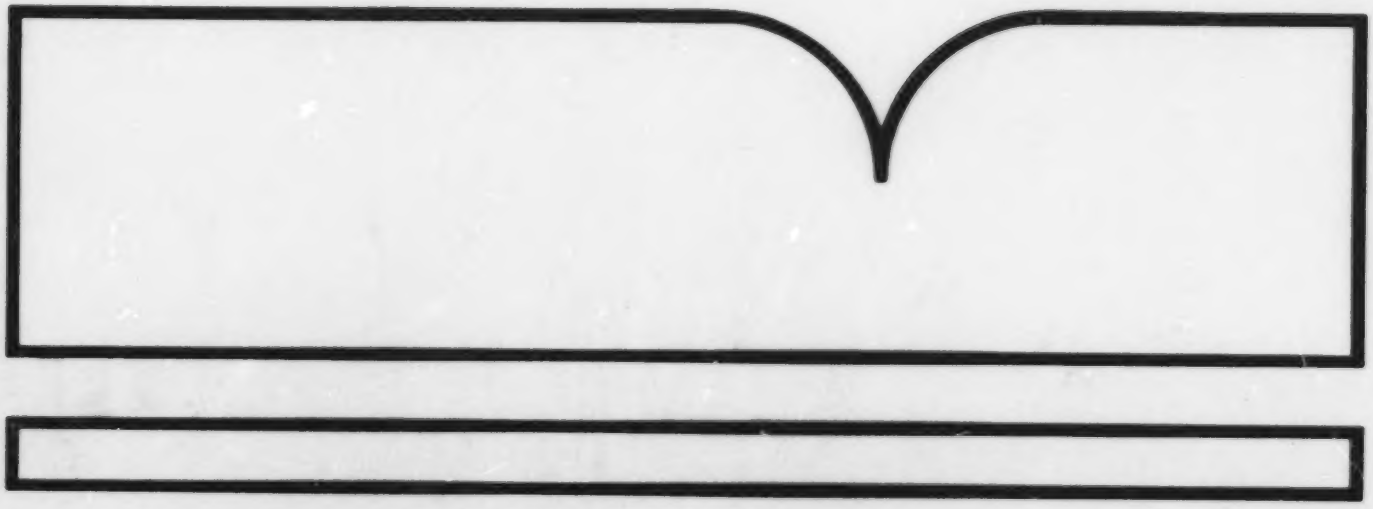
Detection of Oil in Water by a Flame Emission Technique

NUCOR Corp.
Danville, NJ

Prepared for

Environmental Protection Agency
Cincinnati, OH

Jul 81



U.S. Department of Commerce
National Technical Information Service
NTIS

PB81-226185

EPA-600/ 2-81-128
July 1981

DETECTION OF OIL IN WATER BY A FLAME EMISSION TECHNIQUE

by

Manfred Pragar
NUCOR Corporation
Denville, New Jersey 07834

and

D. Stainken
U.S. Environmental Protection Agency
Edison, New Jersey 08837

Contract No. 68-03-0205

Project Officer

U. Frank
Oil and Hazardous Materials Spills Branch
Municipal Environmental Research Laboratory-Cincinnati
Edison, New Jersey 08837

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/		PB81 226185

4. TITLE AND SUBTITLE
Detection of Oil in Water by a Flame Emission Technique

5. REPORT DATE
July 1981

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Manfred Pragar and Dennis Stainken

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
NUCOR Corporation
2 Richwood Place
Denville, NJ 07834

U.S. EPA
Edison, NJ 08837

10. PROGRAM ELEMENT NO.
1BB610

11. CONTRACT/GRANT NO.
68-03-0205

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory - Cin., OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer: Uwe Frank (201) 321-6626

16. ABSTRACT
A flame emission technique and basic instrument design is presented for measuring low concentrations of oil in oil-contaminated water. The flame emission instrument developed in this report would be useful as a detector for petroleum oils. The flame emission technique utilizes the selectivity of the hydrocarbon emission signal (at 431 nm) and oil detection is a function of the total hydrocarbon concentration. Interference of metal ions is avoided by employing steam distillation and condensation techniques to vaporize oil from sample solutions. The prototype instrument successfully detected oil concentrations down to 10 ppm for oils with vapor pressure equal to or higher than No. 4 fuel oils.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chemical Analysis Oils Crude Oil Water Pollution Flame Photometry	Oil Detection Oil-Contaminated Water Petroleum Oils Flame Emission	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

DISCLAIMER

This report has been reviewed by the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report documents the development of a flame emission technique and instrument that can measure low concentrations of oil in oil-contaminated water. The technique, instrumental design, and recommendations for future development are reported. The flame emission instrument developed in this report was proven potentially useful as a remote detector for petroleum oils. This report will be of interest to those individuals involved in routine monitoring of the environment, law enforcement, and industrial wastewater research. Further information about this report is available from the Oil and Hazardous Materials Spills Branch, MERL-Ci, Edison, New Jersey 08837.

Francis T. Mayo, Director
Municipal Environmental Research Laboratory
Cincinnati

BEGIN LAST LINE OF TEXT HERE
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD BEGIN SECTIONS HERE

ABSTRACT

A flame emission technique and basic instrument design is presented for measuring low concentrations of oil in oil-contaminated water. The flame emission instrument developed in this report would be useful as a detector for petroleum oils. The flame emission technique utilizes the selectivity of the hydrocarbon emission signal (at 431 nm) and oil detection is a function of the total hydrocarbon concentration. Interference of metal ions is avoided by employing steam distillation and condensation techniques to vaporize oil from sample solutions. The prototype instrument successfully detected oil concentrations down to 10 ppm for oils with vapor pressure equal to or higher than No. 4 fuel oils.

This report was submitted in fulfillment of Contract No. 68-03-0205 by Nucor Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period December 4, 1972 to December 4, 1973.

0.1"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vi
Abbreviations and Symbols vii
Acknowledgment viii

1. Introduction 1
2. Conclusions 3
3. Recommendations 4
4. Technical Dissertation 5
   - Concept 5
   - Advantages of Flame Emission Method 5
   - Interferences 6
5. System Development 8
   - Improvement of System Sensitivity 10
   - Oil Analysis 11
   - Steam Distillation 13
6. System Testing 20
   - Batch System Procedure 20
   - Continuous System Procedure 23
7. Discussion 34

References 35
Appendices

A. Design Goals 36
B. Description of the Instrumentation used in Flame Emission Spectroscopy 39

FIGURES

Number		Page
1	Conventional steam distillation cell	15
2	Horizontal steam distillation cell	16
3	Jacketed steam distillation cell	17
4	Schematic block diagram of the flame emission detector system	21
5	Steam distillation apparatus linkage to sample and condenser	22
6	Benzene and salt signal variation; signal to noise ratio vs. Nitrogen/Hydrogen ratio	24
7	Flame emission signal of tap water (monitored at 431 nm)	25
8	Flame emission signal of 10 ppm No. 2 fuel oil (monitored at 431 nm)	25
9	Flame emission signal of 40 ppm No. 2 fuel oil (monitored at 431 nm)	26
10	Sampling flow scheme	27
11	Steam distillation cell	30
12	Output signal vs. time for 100 ppm No. 2 fuel oil	31
13	Effect of steam flow rate on the ability of the system to remove No. 2 fuel oil from the sample: steam temperature was 370°C, sample rate was 100 ml/min	32
14	Output signal of 3% salt solution vs. steam pressure	33

TABLES

1	Integrated peak areas of No. 2 and No. 4 fuel oil at various concentrations	28

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD BEGIN SECTIONS HERE

ABBREVIATIONS AND SYMBOLS

ppm	--parts per million
nm	--nano meter
A°	--angstrom
ml	--milliliter
cm	--centimeter
g	--gram
cm^3	--cubic centimeter
mm	--millimeter
UV	--ultraviolet
AC	--alternating current

BEGIN LAST LINE OF TEXT HERE
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD, BEGIN SECTIONS HERE
6-1/2"
3-1/8"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

ACKNOWLEDGMENTS

This report has been compiled by Dr. Dennis Stainken from the original Nucor Corporation technical and progress reports. Explicit recommendations of Uwe Frank, Project Officer, and Leo T. McCarthy, have been added.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 1

INTRODUCTION

Oil pollution is a major problem affecting inland water, coastal waters and the oceans. Hydrocarbons in the aquatic environment generally result from natural, accidental and deliberate pollution. Pollution often results from offshore petroleum production, pipeline leaks and ruptures and tanker transportation.

Disasters involving tankers and drilling rigs are the most spectacular sources of oil spills. Other sources of oil pollution continuously contaminate the aquatic environment. They include leaking oil wells, releases of emulsified oil and water soluble leachates by industries, runoff from roads and streets, exhausts from outboard engines, waste oil from garages, oil from the stacks of ships, bilge oil and seepage. Hydrocarbon input from the air is also believed to be a contributory factor. Additional oil may be derived from sewage sludge and dredge spill which may contain vegetable, animal, and petroleum oils. The presence of biogenic hydrocarbons can complicate analyses at minimal detection levels.

The estimated total annual influx of oil to the ocean is between 5 and 10 million tons. It is of particular importance to analyze the oil concentration in order to avoid adverse effects to humans and their environment. Areas of analytical interest would include discharge outfalls, spill areas, and post spill treatment areas.

Methods used to measure oil concentration in polluted water include fluorescene analysis, gas liquid chromatography, infrared spectrophotometry, ultra-violet adsorption methods, and total carbon analysis. Many of these methods are time consuming and costly. They are used primarily within a laboratory and require sample extraction and preparation. They are often specific for fractions of oils and may be overly selective. The value of the results may be limited due to the complex composition of oils and the sophistication of the methods.

The flame emission method does not require prefractionation of oils before analysis. The method is based on the principle that electrons of elements held in a flame are raised from a ground state to an excited state by the heat energy. If the excited electron drops back to the ground state in one jump, the radiation given off is called a resonance line. If the electron loses its energy in steps, some of the energy may be emitted in the ultra-violet, visible and infrared regions. The wavelength of emitted radiation will differ for each element because of the basic differences of charge and number of electrons. The color and intensity of the emitted radiation may be used for qualitative and quantitative analyses.

The flame emission method has already been used for measuring toxic metals, phosphates, etc. The method has not been used for measuring carbon concentration in water, because of the very low sensitivity of the C-H or C-C emission signal in

BEGIN LAST LINE OF TEXT HERE
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Clin.) (4-76)

comparison to that for metal ions (i.e. Na, Li, Ca, etc.). However, the flame emission method would be useful, for measuring oil pollution, because the hydrocarbon emission signal does not have structure selectivity. In the flame emission method, detection is essentially a function of the total hydrocarbon concentration (e.g., carbon atom concentration).

The objective of this study was to develop the methodology and technology for the detection of oil in water by flame emission spectroscopy. The study involved the development and demonstration of this concept for use as an oil contamination meter. Appendix A describes the design goals and Appendix B contains a complete list of features which were sought in the oil concentration meter.

Several questions had to be resolved before the flame emission technique could be used to detect oil in water. The interference of metal ions (i.e., Na, Fe, etc.) had to be resolved and the sensitivity of hydrocarbons determined. Interference of metal ions was avoided by adapting a steam distillation technique (Goulden et. al, 1973) to vaporize oil from the sample solution. Although the steam distillation separates the water-oil mixture, certain minute amounts of lithium salts were carried over. Condensation techniques were required to remove the large amounts of water vapor generated during steam distillation.

Several types of sample introduction systems were considered, and a dry aerosol method (Veillon and Margoshes, 1968) was chosen. The wavelength selected to monitor oil concentration was at 431 nm (C-H). Another strong emission band at 512 nm (Gaydon, 1957; Robinson and Smith, 1966) is present. However, the use of this band to monitor the hydrocarbon was abandoned because of proximity of sodium D line interference at 589 nm. The initial evaluation of the technique was performed using a batch system. Modifications of this approach permitted continuous analysis of oil water samples.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE

SECTION 2

CONCLUSIONS

The flame emission technique is useful for the detection and quantitation of oil in water. The flame emission instrument developed in this report was also proven potentially useful as a remote detector for petroleum oils. In tests with fuel oils, the sensitivity factors for No. 2 and No. 4 fuel oil appeared to be within 10% of one another. The instrument successfully detected oil concentrations of 10 ppm for oils with vapor pressure equal to or higher than No. 4 fuel oils. However, lower vapor pressure material (No. 6 fuel oil) was detected at decreased sensitivities. Interference from dissolved salts was not detected until the salt concentration approached the concentration of sodium chloride normally found in ocean water. Even at these concentrations, significant interferences were not encountered except at the highest steam rate used for sparging oil with high vapor pressure from the influx water. An instrument of high resolution operated at high temperatures (538°C) appears to be necessary for optimum performance.

Additional development is required for the detection of a broader range of oils. The interference from dissolved salts must be considered in the analysis of low vapor pressure materials, (i.e, crude oils, heavy fuel oils) especially from marine waters. The system will provide a useful means for the remote measurement of oils in both fresh and marine waters if the sensitivity of the system is improved.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 3

RECOMMENDATIONS

The flame emission technique and instrument developed within this report are recommended for further development for use as petroleum oil detectors in oil contaminated water. The relatively simple flame emission method does not require prefractionation of the oils before analysis and will yield satisfactory quantitative results at ppm levels. Further development of the instrumental design will be necessary if it is to be utilized for analysis of heavier than No. 4 fuel oils. It is hoped that an improved instrument incorporating developmental modifications will commercially evolve from the prototype design.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 4

TECHNICAL DISSERTATION

CONCEPT

Flame emission spectroscopy measures the emission produced on combustion in a small hydrogen flame to determine the concentrations of oil in water. Although several emission bands are excited in this process the 431 nm C-H band is the most useful for the analysis of oil in water.

Molecular flame emission spectroscopy can provide sensitive, selective, rapid and accurate measurement of the element to be detected. It has been used to monitor compounds of several non-metallic elements, especially sulfur and phosphorus. Flame emission has been adapted to automated instrumentation for pollution monitoring of chemical warfare agents. Adequate sensitivity has been found with a larger response for hydrocarbons, than for compounds containing other elements in addition to carbon and hydrogen (Robinson and Smith, 1966).

It appeared possible to develop a useful field instrument based on this principle. Flame photometry also seemed to have important advantages over competitive methods. Several commercially available instruments for continuously monitoring water for oil contamination are commercially available.

The most commonly used technical principles applied to oil analysis are fluorescence and absorption spectroscopy. The attenuation of light is measured at wavelengths ranging from the ultra-violet to the infrared. Some workers have also measured oil in water by reflection of incident light by the oil or by determining the ratio of reflected to transmitted light. Other methods include measuring light scattered by oil particles dispersed in water and reduction of electrical conductivity of water by oil.

Some of these methods are entirely non-specific, (i.e., conductivity and light scattering). For other methods, oil must be dissolved (i.e., UV absorption spectroscopy) or the oil must form a film on quiescent water (i.e. reflectance methods). Spectroscopic methods provide a high degree of specificity. This is one reason for the extensive use of UV spectroscopy for monitoring oil in water. However, substances other than oil that are usually dissolved or dispersed in the water will also respond at the analytical wavelength. Flame photometry may solve the problem, because the extent of organic dispersions in water does not affect the measurement in this process.

ADVANTAGES OF FLAME EMISSION METHODS

The literature previously cited indicates a higher flame photometric response for hydrocarbons than for other organic compounds. Introduction of oxygen or chloride into the hydrocarbon structure can reduce emission intensity by a factor of 10 to 25.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE
6-1/2"

One of the requirements for flame emission detection is that the molecules be sufficiently excited to emit radiation; this light is then selectively measured, through regulation of the available excitation energy. This is accomplished by control of flame temperature, flow rates of fuel, oxidation rate, and fuel to oxidant ratio. This is one reason for better specificity in emission than in adsorption spectroscopy.

In flame emission spectroscopy, the maximum intensity of the light emitted by various species is not necessarily observed in the same region of the flame. For some emitters (i.e., sulfur compounds in a hydrogen flame) the emission can be largely confined to a region above the flame cones. For the other emitters, only certain portions of the flame itself are colored. By restricting the field of view, it is often possible to eliminate from measurement the emission from interfering substances. This technique for improving specificity is called limited area flame spectroscopy and is not available in conventional adsorption spectroscopy.

Techniques used in UV spectroscopy to reducing interferences can also be used in flame emission spectroscopy. These methods include the comparison of measurements at analytical and reference wavelengths or measurements made on total samples and on samples with oil removed.

An important advantage of flame emission is that the degree of oil dispersion does not matter because all oil will be detected. In flame spectroscopy, molecular excitation of vaporized oil is measured. The instrument in this study uses an ultrasonic nebulizer to convert the sample to an aerosol. Fine droplets (with a mean diameter of approximately 5 microns) are formed by the oil and water solution in this process. Droplets are then fed into the burner wthere they are easily vaporized. The entire procedure requires only seconds.

The flame emission methodology and instrumentation, can detect oil concentration as low as 5 ppm. To achieve this, several innovations were required: (1) ultrasonic nebulization of the water sample, (2) addition of nitrogen to the hydrogen fuel gas to cool the flame, (3) viewing only a portion of the flame to achieve a high signal above background, (4) sample conditioning whereby much of the sample water is removed from the oil prior to reaching the burner. A detailed description of the instrumentation is described in Appendix B.

INTERFERENCES

Particulates such as paint, wood chips, and scale, do not interfere with detection process. However, they can clog the flow system in the instrument and should be removed by a mechanical filtration prior to nebulization. Air and bacteria do not interfere.

When emitted lines of inorganic species are close to the analytical wavelength, the following methods are available for avoiding interference:

(1) The interfering substance may emit in a region of the flame different from that in which the oil emits. (Oil emits primarily near the base of the burner). In this case it is possible to mask that portion of the flame in which the interference emits and still transmit the radiation emitted by the oil.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.) (4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

(2) When the radiation emitted by interference cannot be prevented from reaching the photomultiplier tube, it is still possible to prevent a response. The emission lines of inorganic ions are very narrow compared to the broad ban C-H emission from oil. To eliminate the ionic line emission from being measured, a chopper with two interference filters is employed. One filter has maximum transmission at the analytical wavelength at which both oil and interference emit. The other filter is selected to have peak transmission at a wavelength at which the interference but not oil emits. These filters are mounted on a wheel between the burner and the photomultiplier tube. The wheel is rapidly rotated by a constant speed motor so that the detector tube will alternately view radiation with and without that from the oil. It is then possible to electronically cancel the interfering radiation.

(3) It is possible to remove ionic species from the water by brief contact of the water with an ion exchange resin prior to nebulization. Contacting water with resin for 30 seconds results in 99% removal of ionic species.

NUCOR has used both filters and ion exchange resin with flame photometric instruments. Interference has not been observed from any anions in water. Signals from cations at high concentrations have been obtained only from calcium and sodium when phosphorus is measured at 525 nm. Both interference could be removed with ion exchange rsins.

Organic substances other than oils are also potential interferences. These would primarily be non-hydrocarbons, and their emission intensity would be expected to be much less than that of oils.

If necessary, the previously described techniques for treating such interferences may be used with a very low temperature flame or a dual channel filter system.

In this study, oil monitors were designed to incorporate custom made interference filters with sharp cut-offs in order to restrict transmitted radiation to wavelengths close to the anaytical band. This also prevented transmission of radiation from species other than carbon compounds.

Further improved discrimination was expected with the use of custom made photomultiplier tubes. The sensitivity of photomultiplier tubes to radiation passed by the interference is a function of wavelength. Peak transmission of the RCA-1P21 tube used in the NUCOR photometric oil monitor is approximately 400 nm. At the time of this study, NUCOR was currently negotiating with a photomultiplier tube manufacturer, EMR Inc., for fabrication of a custom made tube that would peak near the analytical wavelength, (approximately 430 nm) and cut off more sharply at longer wavelengths.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-267 (Cin.)
(4-76)

SECTION 5

SYSTEM DEVELOPMENT

The fabrication of the laboratory study instrument used in the fundamental studies of the flame emission analytical method employed interference filters with peak transmittance at 4300 A and 5145A for measurement of C-H and C bands respectively. An RCA 1P28/V1 photomultiplier tube (to measure the analytical peak emission intensity) and a Mistogen Model EN142 electronic nebulizer, (to present oil in water samples to the burner) were also used. A burner was assembled from components on hand. It was installed with other available and necessary components (aspirator, ignitor, etc.) in a cabinet for use in initial evaluations. A NUCOR fabricated variable voltage power supply and a Keithley Model 600B electrometer were used to supply voltage to the photomultiplier tube and to measure photomultiplier output current. A Gast Model 1531 oil-less compressor was chosen to provide the driving air for the aspirator.

An electrically heated glow ignitor was fabricated from a coil of platinum wire. However, this ignitor did not function reliably. In earlier work, a spark ignitor was used. A high voltage was applied between the capillary tube which supplies the hydrogen fuel and the stainless steel nozzle that the hydrogen fuel and the stainless steel nozzle that separates the combustion chamber from the emission zone of the burner. A spark jumping across a gap of a few millimeters between these two pieces ignited the flame. This procedure was suitable for a phosphorus or sulfur detector in which the capillary was placed behind the emission zone for purposes of shielding the photomultiplier tube from the flame. For oil monitoring however, it was necessary to view the flame directly which would require that hydrogen capillary be advanced into the emission tub. Therefore, the distance between the nozzle and the capillary would be too great for the ignition to occur. A spark was therefore used for ignition while the capillary was in a retreated position. After ignition, the capillary tube was advanced into the emission zone. Although inconvenient, this method of igniting sufficed until optimum burner geometry was established.

Initial measurements were made using benzene vapors in air as a source of carbon containing radicals. These samples were used to measure C-H emission of 4315 A° (or C emission at 5165 A°) and to investigate the effect on emission intensity of such operating parameters as fuel and combustion air flow rates, analytical wavelength, and photomultiplier tube supply voltage. At the same time, it was possible to avoid complications (flame noise, cooling of the flame) caused by water droplets.

The following method was used for introducing benzene vapors into the air stream supplied to the burner. A piece of filter paper was rolled up and inserted into a short length of 6 mm Pyrex tubing. A few drops of liquid benzene were put on the paper. One end of the tube was attached to a cylinder of compressed air, and the other end was attached to a hypodermic needle. During measurements, the

hypodermic needle was placed into the sample inlet. Air was passed at a low flow rate through the tube and entrained benzene vapors. At the sample inlet, this benzene containing air was diluted by the much larger air flow introduced into the burner to support the combustion of the hydrogen. It was assumed that the air from the hypodermic needle was saturated with benzene vapors. From knowledge of the two air flow rates and the ambient temperature, it was possible to calculate the benzene vapor concentration.

Some measurements were made from observation of the flame characteristics. A blue-green emission was observed in and beyond the flame when benzene vapors were added to the air stream, and the burner was set a hydrogen flowrates of about 150 to 1600 ml/min with air flow rate of 600 ml/min.

Measurements were made with approximately 10 ppm benzene in air, which could be easily detected. At a constant air flow, the best response was obtained at a hydrogen, flow rate of 350-400 ml/min. Measurements designed to determine the effect of operating parameters on performance were continued with approximately 15 ppm benzene vapor in air.

Using hydrogen at 350-450 cc/min. the air flow rate for combustion was varied between 700 and 1700 ml/min. At high air flow rates, it was necessary to increase the hydrogen flow above the normally used value of 350 ml/min in order to maintain a stable flame. The background current which depends greatly on hydrogen flow was also insignificantly affected by changes in air flow rate.

The burner was usually cooled by passing a portion of the air from the compressor over the exterior burner surface in the vicinity of the flame. When the burner was operated in this manner, a thermocouple on the outside of the burner indicated a temperature of approximately 70°C. When the burner was not cooled, the temperature rose to 120°C. Cooling was beneficial, dampening the signal noise. Consequently, the signal to noise ratio and detectability were improved.

Measurements were made with an interference filter exhibiting peak transmission at 4300°A. The response was significantly greater when the lower wavelength filter was used. This filter was designed to measure C-H emission which is most intense at 5145°A.

Photomultiplier currents were measured with a Keithly electrometer. In the instruments under development, an electrometer circuit with range switch, which is used in a NUCOR radiation monitor was to be included. The necessary components capable of measuring currents between 10^{-5} and 10^{-9} amps were assembled. The range switch permits selection of full scale meter ranges of 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, and 10^{-9} amps. The circuitry was tested with currents applied from a battery. At high currents of 10^{-5} to 10^{-7} amps, the circuit behaved correctly. At lower currents the same signal applied to different ranges could not be measured correctly. It was eventually determined that AC pickup interfered with the measurements at low currents. This was eliminated by appropriate modification of the circuits, and satisfactory performance was subsequently observed.

Preliminary emission measurements were made with hydrocarbons dissolved in water. In the first experiment, a saturated solution of pentane in water was used. A

large signal was obtained on introducing an aerosol sample into the burner. This signal lasted only a few seconds, although aerosol generation was continued.

When the nebulizer was disassembled it was observed that the original strong hydrocarbon odor had completely disappeared from the solution left in the aerosol generator. Because of the violent agitation accomplying aerosol generation, the hydrocarbon was apparently removed from the nebulizer at a faster rate than water. This resulted in an increased pentane concentration during the aerosol phase.

Subsequent experiments were performed with solutions of 50 ppm heptane or 100 ppm benzene in tap water. Small signals that did not decrease to the background value were obtained with these solutions. However, nebulization reduced the intensity of the odor of these solutions.

The effect on hydrocarbon emission intensity of singularly varying several operation parameters (one at a time) was studied. Responses were best when a relatively large and hot flame was used. This was achieved by increasing the size of the flame jet, heating the exhaust aspirator, and not cooling the flame. In all cases, the hydrocarbon emission represented a small increase above that of the background observed with water without added hydrocarbon. Improved performance with a hotter flame may be caused by more efficient volatilization of the sample. A comparison of data obtained with air and water samples containing benzene showed the system to be almost twice as sensitive to a given amount of benzene in air compared to benzene in water.

Limited area measurements were also made with an interference filter with peak transmission at 5145 A. However, the response was much smaller than was observed with the lower wavelength (i.e. 4300A) filter.

The response of various concentrations of benzene in tap water were also examined by the limited area technique. Although the signal obtained was much improved, it was not steady because of a gradually decreasing hydrocarbon concentration in tap water during nebulization.

IMPROVEMENT OF SYSTEM SENSITIVITY

The C-H sensitivity was highly improved by measuring the limited area of the flame, but further enhancement of the signal to noise ratio was needed for the detection of hydrocarbon concentrations of less than 10 ppm in water. Therefore, the following modifications of the burner system were made:

(1) With the H_2 flame pointing downward, the sample was introduced upward into the flame.

(2) The sample was introduced from the top of the flame.

(3) A non-shielded oxidizing flame without glass chimney was used.

(4) The N_2-H_2 flame was diffused.

The results obtained from arrangements (1), (2), and (3) were not as good as those with the flat burner. A N_2-H_2 diffusion flame, however, produced a 4-fold increase in the emission signal even when a shielded burner was used.

To prevent the loss of sensitivity when benzene in water aerosol was directly injected into the burner, the benzene aerosol sample was passed through a glass tubing preheated at approximately 250°C and then cooled in an air condensor. This had a trap at the bottom for the removal of condensed water. The detection limit for benzene in distilled water was improved to 30 ppm by the combined modifications of nitrogen diluted hydrogen flame and aerosol sample heating-condensing techniques. It was clear that the method used to introduce the aerosol sample into the burner greatly affected C-H sensitivity.

In order to optimize the C-H signal, a combination of (1) N^2-H_2 diffusion flame, (2) a flat burner, and (3) plane mirrors around the burner to reflect additional light to the photomultiplier tube were investigated. In addition, the hydrogen flame was shielded by a 0.6 cm slit as previously described, permitting a limited area of the flame to be viewed by the photomultiplier tube.

Generally, the injection of a 15 ppm benzene in air sample into the burner, caused a doubling of the output signal under the limited area measurement. The output signal doubled again when a flat burner was used, and tripled if three flat mirrors were mounted around the burner. The most important factor in the flame detector was the use of a N_2-H_2 diffusion flame which decreased the background of the flame and improved the signal ten times. These modifications improved the sensitivity 120 times compared to earlier measurements of benzene in air.

OIL ANALYSIS

An oil dispersion was prepared by mixing 0.2 ml of No. 2 fuel oil in one liter of distilled water, followed by agitation with an ultrasonic probe for 10 minutes. The colloidal mixture was allowed to stand for 15 minutes in a separatory funnel before the lower part of the dispersion was collected in a stock bottle. A small sample of the oil dispersion was then extracted with Freon 113 and the oil concentration determined with an IR double beam spectrometer (Gruenfeld and Frederick, 1977).

In modification of the technique of Veillon and Margoshes (1968), aerosol samples generated in the Mistogen Electronic Nebulizer were passed through a glass tube wrapped with heating tape and heated to 250°C. The samples were then passed through a Friedrichs condenser and into the burner. Using this arrangement with the instrument, modified with a N_2-H_2 diffusion flame, flat burner, plane mirrors and a 0.6 cm slit, it was possible to detect 4 ppm benzene or 10 ppm of No. 2 fuel oil in distilled water. Measurements with a 5 ppm oil solution also showed a small positive signal. We began work on eliminating responses from interfering substances present in non-distilled water.

An oil in tap water solution was introduced into the burner under the same conditions as previous tests with distilled water solutions. Even a No. 2 fuel oil in tap water sample was not detectable, presumably due to emission interference from metals in tap water. When an oil in tap water solution was introduced into the burner,

the signal of the C-H band at 431 nm was masked by these metals. Experiments to remove interfering metals without affecting the oils were attempted by passing the oil in tap water solution through an ion exchange column. This failed because the organic ion exchange resin had a strong affinity for the oils.

A modification of this metal ion removing procedure was performed by connecting a dry cation exchange resin column between the sample injection port and the condensor of the sample introduction system. It was found that a dry benzene vapor sample was able to pass through the column without losing its sensitivity. However, some signal from the No. 2 fuel oil in tap water sample was still lost to adsorption of the oil on the resin. Only 70 ppm of No. 2 fuel oil in tap water was detectable by this method. We also tried using Bio-Rad Zp-1 (100-200 mesh) inorganic cation exchange crystals instead of the organic resin in the column between the condenser and burner. In order to increase the mobility of oil in the crystal column, the crystal column was preheated to 250°C. The detection limit was lowered to 50 ppm using this method.

A small portion (1-2 g) of the cation exchange resin was also mixed with the sample solution and stirred on a magnetic stirrer, prior to nebulization. It was found that after stirring for one minute, 99% of the metals were removed in water, but also about 50% of the oil was removed from a 50 ppm oil in distilled water emulsion. The detection limit of oil in tap water was lowered by this technique to 20-30 ppm.

It was then thought that by reducing flame temperature through addition of nitrogen to the fuel gas, the emission of metallic ions (i.e. sodium and calcium) could be reduced and their interference minimized. Measurements of C-H, tap water and sodium response were made in flames in which the N_2 to H_2 ratio was varied from 2 to 5. Within this range, the C-H emission was twice as great at the highest N_2 to H_2 ratio than at the lowest. In contrast, sodium and tap water responses were about 25% greater at the lowest N_2 to H_2 ratio than at the highest one. Therefore, operating the flame at a high N_2 to H_2 ratio (low flame temperature) increased the C-H response and lowered the metal ion response.

These results indicated that C-H response and discrimination against metal ions could be improved by operating under cool conditions. Unfortunately, even at the highest N_2 to H_2 ratio at which stable flame conditions could be achieved (a N_2 to H_2 ratio of about 5), the sodium response was still very strong.

Both narrow band interference filters and broad band pass filters were tried individually and in combinatin to occlude sodium emission. A significant improvement was not observed over the commonly used Baird-Atomic filter. The use of a Baird-Atomic filter in conjunction with a didymium filter designed to block the sodium line at 589 nm also did not result in improvement. The data indicated that sodium was a much more serious interference than calcium.

The following steps were taken to eliminate sodium interference. A custom made filter with sharp cut-off was ordered from Baird-Atomic. Although the standard filters used previously transmitted 0.1% outside the band pass, the custom made filter transmitted 0.001% outside the band pass (at the expense of some loss of transmission at the analytical wavelength). In addition, negotiations were started with EMR, Inc. for the fabrication of a custom made photomultiplier tube with a cut-off at a much

lower wavelength than the 650 mm cut-off of the RCA 1P21 tube used previously. It was thought that the intensity at 590 nm could be decreased 100 to 1000 times. If these gains could be realized, the sodium emission would be blocked from detection and measurement of oil in sea water would be feasible.

Measurements with the improved instrument using 6 concentrations between No. 2 fuel in distilled water showed a linear response over the entire range. It was also found that the same response was obtained for equal concentrations of No. 2 and No. 4 fuel oils in distilled water.

The methods used to decrease the metal (sodium) emission interference from tap and salt water were as follows:

A. to use a non-commercial special wavelength selective photomultiplier tube with a sharp decrease in response beyond 500 nm.

B. to use a high transmission but very narrow band optical filter with specially sharp transmisson cut-offs.

C. limited area measurement of the flame

D. to separate the oil from salt water by either physical or chemical methods.

The responses of RCA-1P21, RCA-1P28, and several specially made EMR photomultiplier tubes were then compared for a better oil signal in tap water. A variety of Corning and Kodak optical filters with sharp long wavelength cut-offs to prevent detection of the 589 nm sodium line were also tested. Combinations of these optical filters and photomultiplier tubes decreased the sodium interference in tap water but did not eliminate it. The sodium emission spectrum still exhibited a small band in the reducing flame at 440 nm which appeared in the inner cone of the flame. This was apparently the principal interference, rather than the 589 nm line.

STEAM DISTILLATION

The strongest C-H flame emission signal was found at a height of 6-7 nm above the burner tip in the outer cone. Construction difficulties prevented the complete separation of the inner and outer cone of the diffusion flame. A steam distillation method which resulted in the successful determination of 5-10 ppm of oil either in distilled or tap water was therefore devised. Steam was passed through the oil containing water sampie. The sample was then passed through a preheater-condenser to eliminate much of the water prior to reaching the burner, as previously described. With this arrangement, the same background response was obtained from distilled water, tap water, and a 1% sodium chloride solution; and 5 ppm of oil in tap water gave a positive response above the background.

Plotting the area under signal peaks against concentrations generally yielded a linear relationship for the No. 2 and No. 4 fuel oils. Some difficulty was encountered in working with a No. 6 oil because it has a high boiling point and therefore more time was required to remove No. 6 oil from solution. Apparently, the steam temperature greatly influences the rate of distillation and to accomplish this efficiently a higher

temperature steam was required. A high temperature steam would presumably vaporize oils much faster and a narrow signal band would be obtained. The peak height rather than its area would then be used for the oil concentration determination.

In order to detect the oil concentration in a continuous flow system, a conventional distillation cell, shown in Figure 1, was made for this purpose.

A preheated sample solution was introduced into the distillation cell (in Figure 1) through the bottom (A) and heated steam was fed through a tube (C) to the bottom of the cell. The port at (B) served to maintain constant sample volume in the cell. The sample flow rate was adjusted to about 0.3 cc/sec. The vapor outlet (E) was connected to a water condenser, which in turn was connected to the H_2-N_2 burner. This method was sensitive only at the 20-30 ppm level for No. 4 fuel oil. The solution from the drain (D) was collected and some oil was still left in the waste suggesting that more efficient oil volatilization was required for the continuous measurements. It seemed reasonable that a long horizontal cell might serve this purpose. An example of a horizontal steam distillation cell is shown in Figure 2.

The cell had to be long enough to permit vaporization of all the oils during sample flow from A to B.

In reporting the linear relationship between the area of the recorder response and the oil concentration for a batch system, the average response for the No. 2 fuel oil was about 25% higher than for the No. 4 fuel oil. The data indicated the importance of increasing the temperature in the distillation cell in order to more efficiently volatilize the oils.

A horizontal distillation cell 23.75 cm long and 3.12 cm in diameter was prepared, and a preheated solution was introduced into the sample cell along with hot steam at the flow rate of 0.4 cc/sec. Using this conventional method, approximately 10 ppm of No. 4 oil in tap or salt water solution was detected.

The passage between this distillation cell and the condenser was too small to pass the oil vapor and the steam which resulted in a somewhat noisy signal. Extra large holes were then made on the top of the distillation cell so that a steady and homogeneous steam-air mixture could be obtained. The whole distillation cell was covered with a 53 mm diameter cylinder jacket (Figure 3).

With this system, a 1 ppm benzene in air sample was easily detected, but a 5 ppm oil in water sample flowing continuously could not be detected. Detectability of No. 4 fuel oil was still at 10 ppm. Examination of the solution flow out of the drain showed that the No. 4 fuel oil was not completely removed from the water by steam distillation. The temperature of the inlet steam was measured to be 324.7°C which is far below the boiling point of the No. 4 and No. 6 fuel oils.

In general, detection of No. 2 and No. 4 fuel oil was possible down to 10 ppm when the steam temperature was 318°C. Number 6 fuel oil, having a lower vapor pressure than either No. 2 or No. 4 fuel oils, required an increased steam temperature in order to achieve the 10 ppm detection level. The steam distillation rates are dependent on the vapor pressure of the components to be removed from solution.

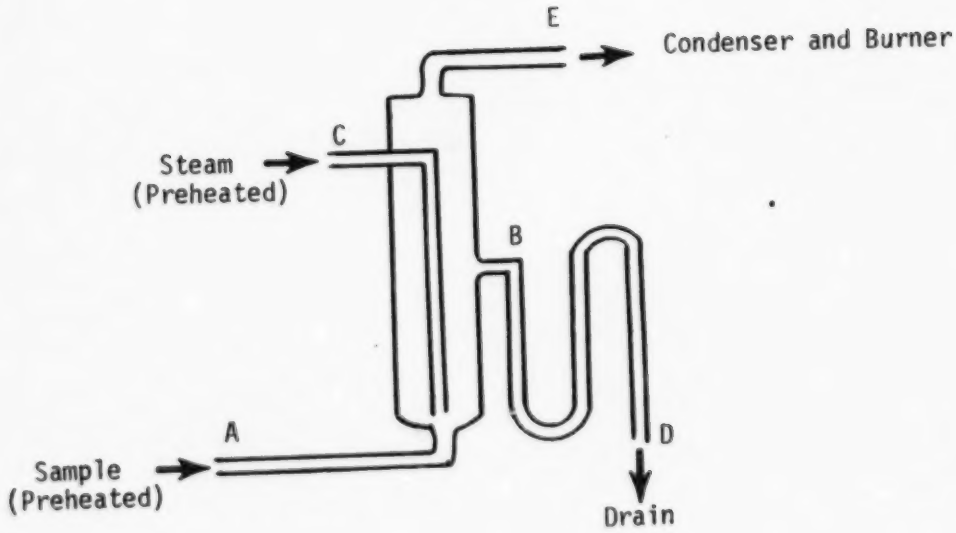


Figure 1. Conventional steam distillation cell.

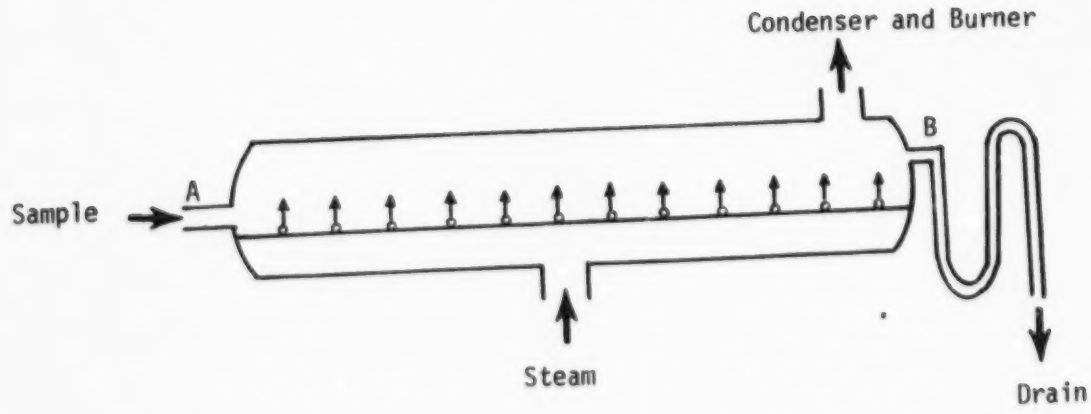


Figure 2. Horizontal steam distillation cell.

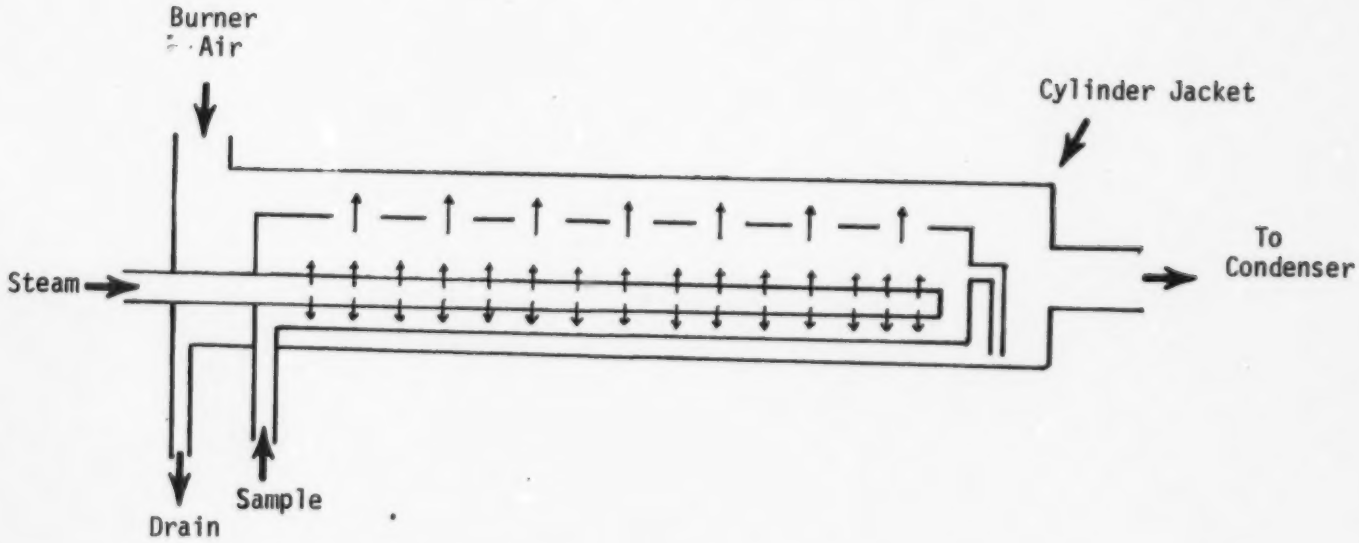


Figure 3. Jacketed steam distillation cell.

Although most of the hydrocarbons could be steam distilled at temperatures lower than their boiling points, the steam distillation rate was highly dependent on the component vapor pressure at the temperature of the applied steam. Therefore, a steam generator and superheater were utilized to increase the steam temperature to a range of 486°C to 542°C.

It was observed during operation with the high temperature steam that an unexpected noise signal resulted when high temperature steam (greater than 318°C) was passed through a 0.5%-3% salt solution. Temperature scanning of the 3% salt solution showed that a small amount of salt was driven out of solution when the steam temperatue exceeded 318°C. The noise level from the salt depended on the salt concentration. Therefore, although a 542°C steam temperature removed oil in solution more rapidly than 318°C steam, oil concentrations of less than 30 ppm were not readily detected due to the increased background (salt) signal.

It was therefore necessary to remove the salt from the aerosol generated by steam distillation at higher temperature before introducing the aerosol into the burner. It was found that either a gas trap half filled with glass beads or a screen mounted slightly above the sample solution significantly reduced the noise from the belt. Salt could be removed by the above methods because:

1. Salt is soluble in water but oil is not. When a mixture of oil and salt containing vapor is passed through a water trap, salt is removed by a dissolving process. However, small amounts of oil are also removed by condensation and adsorption.

2. When tap water was dropping onto a hot plate, a very large signal was obtained from the atomization of salt. A screen prevented the water from splashing onto the hot steam pipe and thus the formation of salt aerosol was reduced.

NUCOR subsequently developed the following techniques toward fabrication of the required instrument:

1. Establishment of a continuous sample flow system employing the steam distillation technique.

2. Optimization of system parameter.

3. Assembly of prototype instrument.

A continuous sample introduction system was established using a small peristaltic pump for introducing the sample into the distillation cell. Additional improvements were made in the control and measurement of the steam flow rate and temperature, and the sample flow rate. With the continuous system established, a series of sensitivity and linearity measurements using No. 2 and No. 4 fuel oils were conducted.

This series of measurements resulted in linearity within 10% attained for No. 2 and No. 4 fuel oil. Samples ranging from 13 ppm to 250 ppm were used, and favorable linearity and sensitivity resulted.

A more efficient vaporation of oil contained in the sample was sought. Reasonable performance was obtained with high temperature steam, but the higher heat content of the resulting vapor necessitated the use of a more efficient condenser for optimum performance. The system was modified to include a high performance condenser.

Results from the steam distillation cell were encouraging. To evaluate the system more precisely, attempts were made to improve sample preparation and to develop a simple calibration technique. A laboratory stirrer was found to be convenient for mixing No. 2 and No. 4 fuel oils, and a sonifier was used to prepare homogeneous No. 6 fuel oil samples.

The set point precision of the flow controller regulating the detector flame was not satisfactory when distillation cell efficiency was evaluated. Small variations in hydrogen flow rate caused variations in detector sensitivity; a calibration scheme was, therefore, required to evaluate system sensitivity before distillation cell efficiency was evaluated. The calibration technique consisted of a metered flow of air through a wick saturated with benzene. The air carried the benzene to the detector reproducibly. Calculations involving the air flow rate, the benzene vapor pressure and temperature enabled an accurate determination of system sensitivity.

SECTION 6

SYSTEM TESTING

EXPERIMENTAL SYSTEM BATCH SYSTEM PROCEDURE

The flame emission oil detector system is illustrated in Figure 4. Sulfuric acid acidified tap water was used as the source of steam in this procedure. The tap water was acid treated and boiled before each measurement to remove any carbon dioxide or bicarbonate. The sample flask contained 40-50 ml of sample per measurement. A Baird-Atomic narrow band filter with maximum transmission at 431 nm, band width at 10 nm and 85% transmission at peak wavelengths was used.

The tubings and glassware were insulated with asbestos. The steam distillation was performed in a 125 ml Erlenmeyer flask fitted with a 5 cm diameter round glass trap (Figure 5). The steam vapor was connected to a Friedrich condenser shown in Figure 5, to allow ambient air to flow into the condenser without difficulty.

The stainless steel burner was supplied by a mixture of hydrogen and nitrogen gas. The gas flow rate was regulated with two Matheson flow meters. The 1 x 7 mm flat burner was centered in a 1.9 cm diameter quartz tubing chamber. The flame was viewed 1 mm above and 6 mm below the burner tip with the flame upside down for maximum sensitivity.

The tests were conducted to evaluate the technique and system utilizing experimental benzene and oil standard solutions. These standard solutions provided a means of calibrating and evaluating the system.

The Benzene Standard

A 12 cm long, 5 mm diameter glass tubing was filled with cotton (to a depth of about 10 cm) and wetted with benzene. The benzene standard tubing was connected to a flow meter which was attached to an air tank. Air, flowing over the benzene-soaked cotton became saturated at a concentration corresponding to the vapor pressure of the compound at room temperature. The flow meter was adjusted so that a constant amount of benzene was vaporized at any temperature.

The Oil Standard Solution

Standard oil solutions (of No. 2, 4, and 6 fuel oils were prepared fresh and salt water. Stock oil emulsions were prepared by sonification with a Branson sonifier cell disruptor (Model W-185) and quantified by infrared analysis (Gruenfeld and Frederick).

A. Steam generator (500 ml Erlenmeyer Flask)
B. Trap
C. Sample flask (125 ml)
D. Friedrich condenser
E. Burner (1 x 7 mm, flat stainless steel)
F. Aspirator
G. Baird atomic narrow band filter
H. RCA IP-21 Photomultiplier tube
I . High voltage DC supply
(J. Fluke Mfg. Co., Inc., Model 412A)
J. Keithley 610B Electrometer

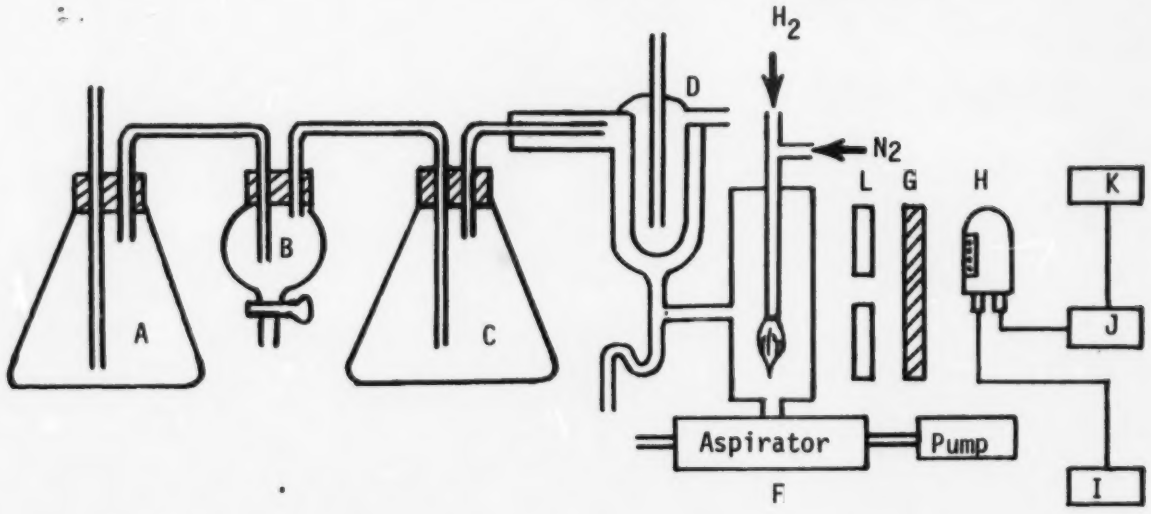


Figure 4. Schematic block diagram of the flame emission detector system.

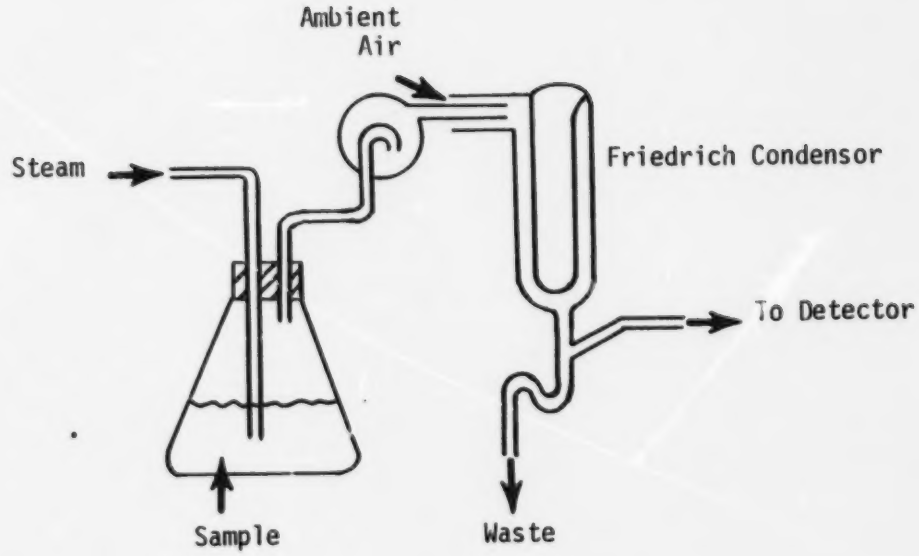


Figure 5. Steam distillation apparatus linkage to sample and condensor.

RESULTS

Flame sensitivity was measured with a 2 mm diameter cylindrical burner. The sensitivity near the burner tip was about four times higher in comparison to the sensitivity near the top of the flame. The sensitivity of the diffusion flame was also examined. The N_2 to H_2 ratio did not have much effect on the most sensitive flame area. However, the benzene detectability was increased with an increasing N_2 to H_2 ratio which optimizes the C-H signal. At a H_2 to N_2 ratio of 5:1, a maximum response for C-H emission was obtained. The emission response of No. 2 and 4 fuel oils was linear and equal for both oils (from 5-90 ppm in distilled water).

Benzene and salt signal variation with N_2 to H_2 flow rate and the signal for tap water and 120 ppm sodium ions atomized with a Mistogen Nebulizer are shown in Figure 6. The aerosol was preheated before injection into the burner compartment. This data indicates that salts must be removed before injection into the burner. The burner must use a diffusion flame to minimize interference. A nitrogen flow rate of 350 cc/min and hydrogen flow rate of 100 cc/min gave the best performance. A quartz viewing tube was required to prevent interference signals from the sodium normally found in glass.

The effect of steam distillation of tap water is shown in Figure 7. The curves were obtained with 40 cc of tap water in a 125 ml Erlenmeyer flask. The sharp peaks are caused by desorbed carbon dioxide. The sensitivity of the flame emission detector to carbon dioxide could be explained by the formation of a C-H radical which was observed repeatedly. The signal of tap water was significant and reproducible.

Figures 8 and 9 illustrate the characteristic signals of No. 2 fuel oil. The integrated peak areas of various concentrations of No. 2 and No. 4 fuel oils are shown in Table 1.

SAMPLE PREPARATION - CONTINUOUS SYSTEM PROCEDURE

Oil-water samples were prepared by placing a measured quantity of oil in approximately 200 ml of tap water to prepare 100 ppm stock dispersions. A syringe was used to dispense the oil. Oil-salt water samples were prepared using 3.5% table salt, tap water and oil. The oils employed were Nos. 2, 4, and 6 fuel oils, and a Waring Blender was used to emulsify oil-water mixtures. Replicate samples of the resultant dispersions were analyzed to determine their homogeneity and reproducibility. Analysis revealed a difference of approximately $\pm$ 4% between replicates. Subsequent dispersions were not analyzed, although the same procedure was used in making the samples.

EXPERIMENTAL SYSTEM

A peristaltic pump metered the oil sample into the steam distillation cell. Figure 10 illustrates the sampling flow scheme. Flow rates from 50 ml/min to 150 ml/min were obtained by varying the rotational speed of the pump. Precise control of flow was not possible with this setup, and during critical experimental runs the flow was monitored continuously with a burette. The sample was added to a 50 ml burette which discharged into the peristaltic pump. Measurement of the time interval to inject 20 ml gave an accurate indication of the flow.

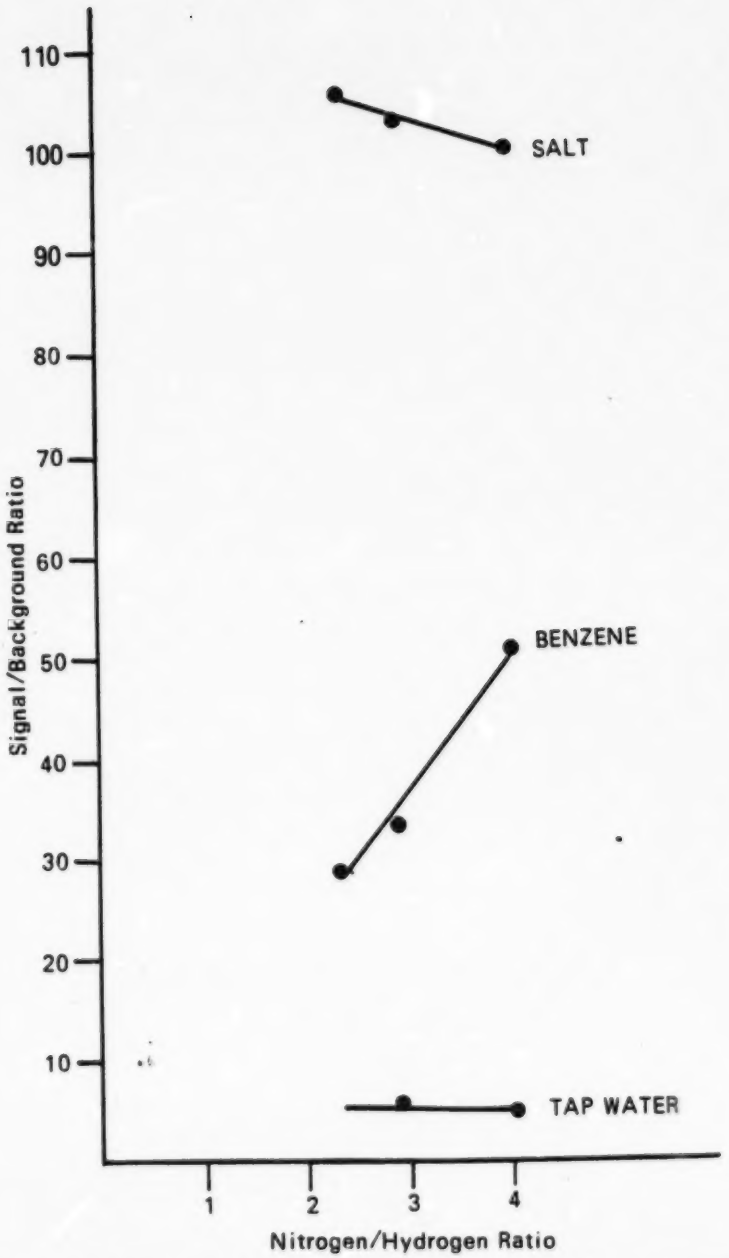


Figure 6. Benzene and salt signal variation: Signal to noise ratio vs Nitrogen/Hydrogen ratio.

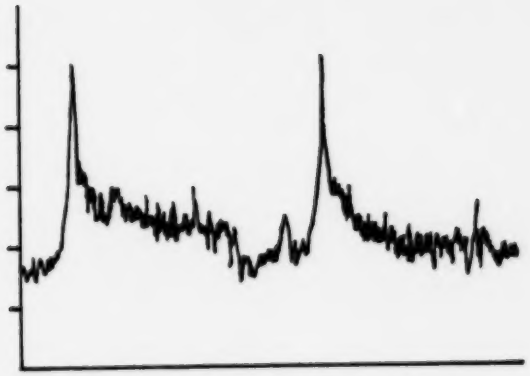


Figure 7. Flame emission signal of tap water (monitored at 431 nm).

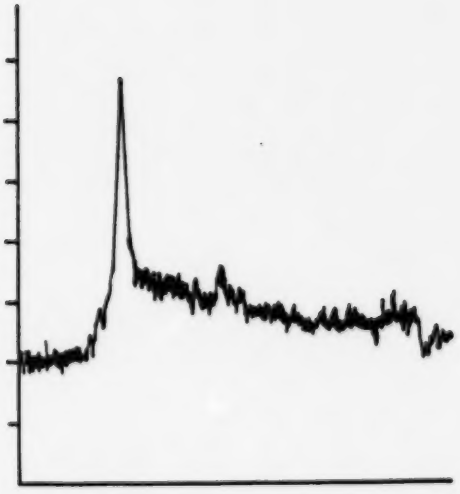


Figure 8. Flame emission signal of 10 ppm No.2 fuel oil (monitored at 431 nm).

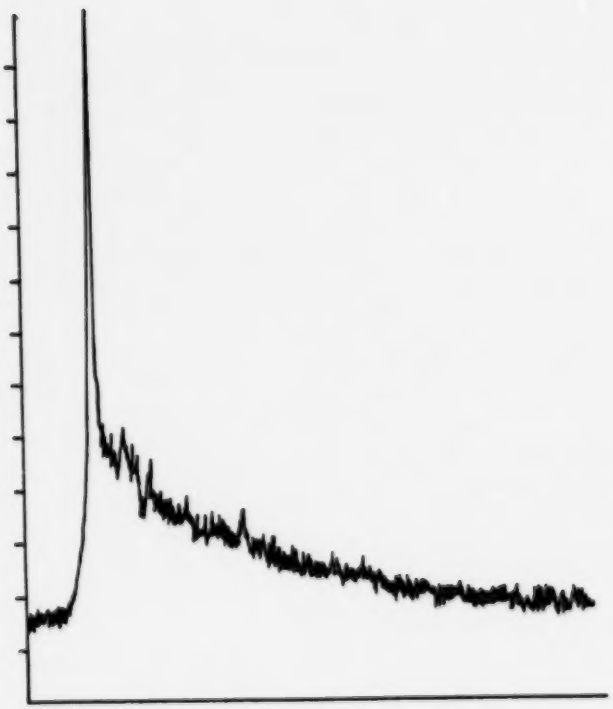


Figure 9. Flame emission signal of 40 ppm No. 2 Fuel oil (monitored at 431 nm).

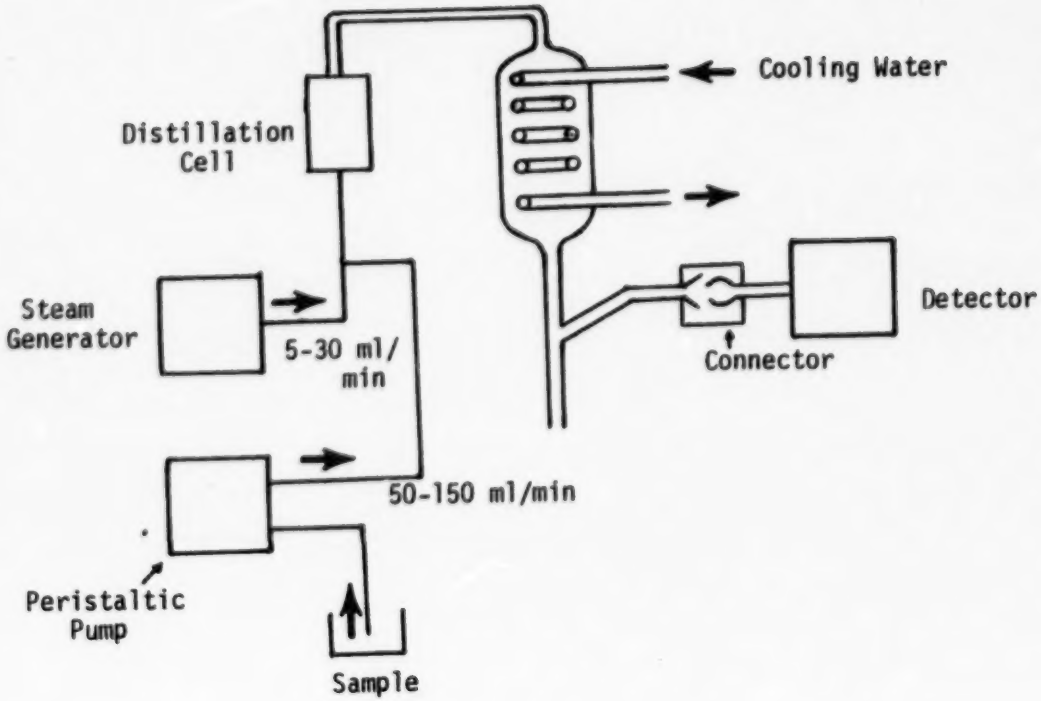


Figure 10. Sampling flow scheme.

TABLE 1. INTEGRATED PEAK AREAS OF NO. 2 AND NO. 4 FUEL OILS AT VARIOUS CONCENTRATIONS

Concentration of sample	No. 2 fuel oil	No. 4 fuel oil
Blank	1.03	1.13
10 ppm	2.13	1.63
15 ppm	3.53	3.15
20 ppm	7.65	6.31
30 ppm	10.40	9.70
40 ppm	13.20	12.20
50 ppm	13.00	13.00
60 ppm	16.50	13.80
70 ppm	20.10	19.50
110 ppm	32.00	30.70
140 ppm	41.60	42.00
220 ppm	64.70	63.50

The steam distillation cell is indicated in Figure 11. Steam was supplied from a commercially manufactured generator. Approximately 5-30 ml/min (condensate) were used to heat and strip the oil from the sample. The amount of steam supplied was altered by varying the power to the generator. Greater extraction efficiencies (90%) were obtained at flow rates of 10 ml/min and higher.

The oil laden steam was cooled in a Friedrichs condenser and detector as described in earlier sections of this report. Steam rates higher than 30 ml/min could not be handled by this condenser.

RESULTS

Typical output data is indicated in Figure 12 at a steam input rate of 30 ml/min. A concentration of 100 ppm of No. 2 fuel oil was used in the sample. Similar results were obtained with No. 4 fuel oil at the highest steam rates, but the sensitivity of the instrument for No. 6 fuel oil was considerably lower.

Figure 13 illustrates the effects of steam flow rate on the ability of the system to remove No. 2 fuel oil from the sample. The background signal of Figure 10, may be due to carbon dioxide or bicarbonates present in the water. The oil signal is directly proportional to the steam flow rate up to approximately 30 ml/sec. At this point the increase in signal is minimal at the higher flow rates. Similar data with No. 4 fuel oil was obtained. Number 6 fuel oil required extremely high steam rates, (30 ml/min), to obtain any signal at all.

Operation of the instrument was also tested employing the 3.5% water samples. The salt signal obtained at high steam rates is shown in Figure 14. This data was obtained from a distillation cell without a baffle. The baffle illustrated in Figure 11 suppressed the salt signal to very low values until steam rates in excess of 50 ml/min were used. The sensitivity of the instrument for No. 6 fuel oil did not increase at these flow rates, and therefore they were not utilized.

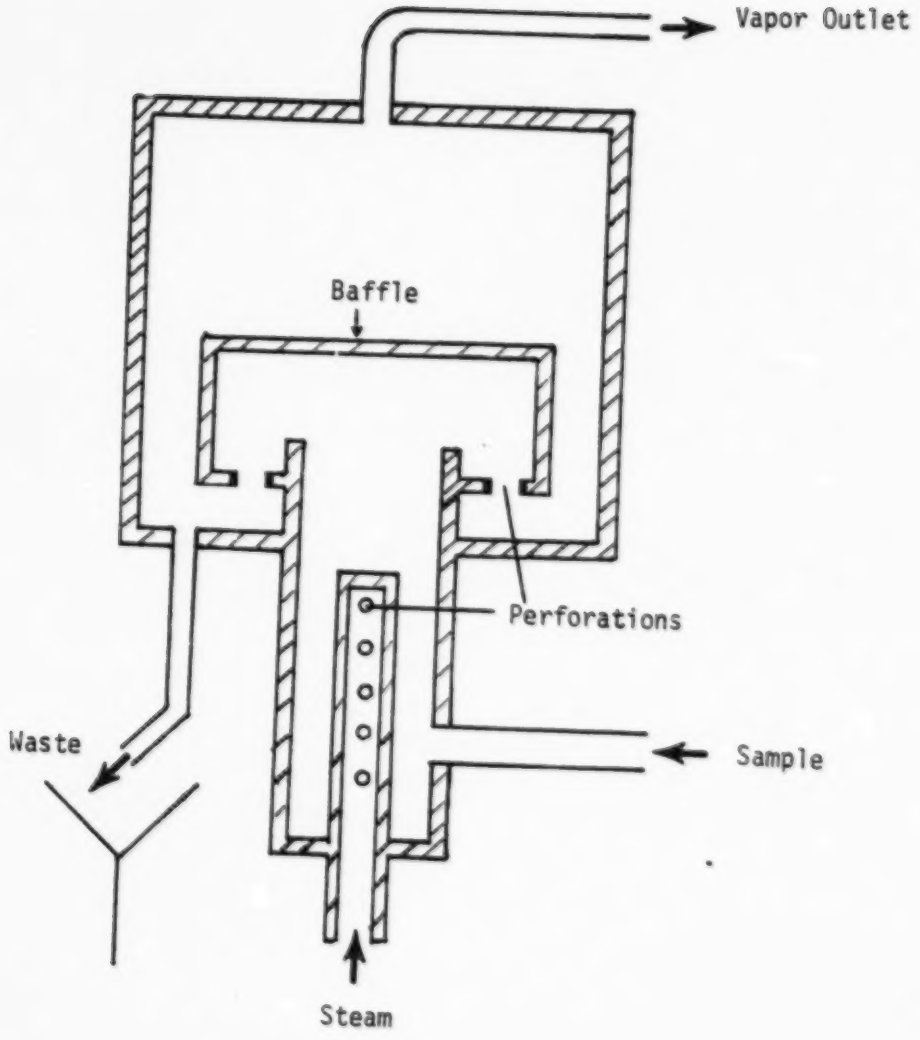


Figure 11. Steam distillation cell.

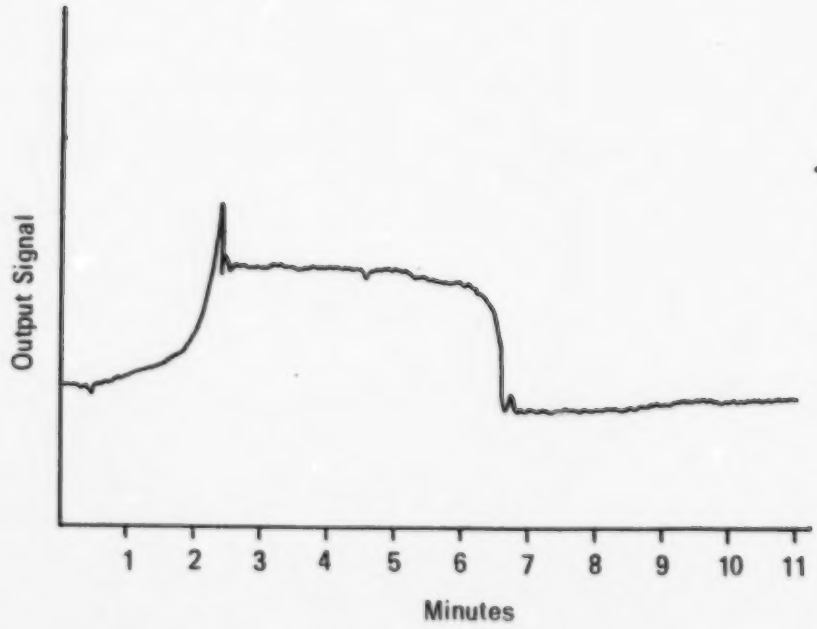


Figure 12. Output signal vs Time for 100 ppm No. 2 fuel oil . Sensitivity was 10 x 10^{-9} amps full scale with 100 ml/min of sample flow - steam distillation.

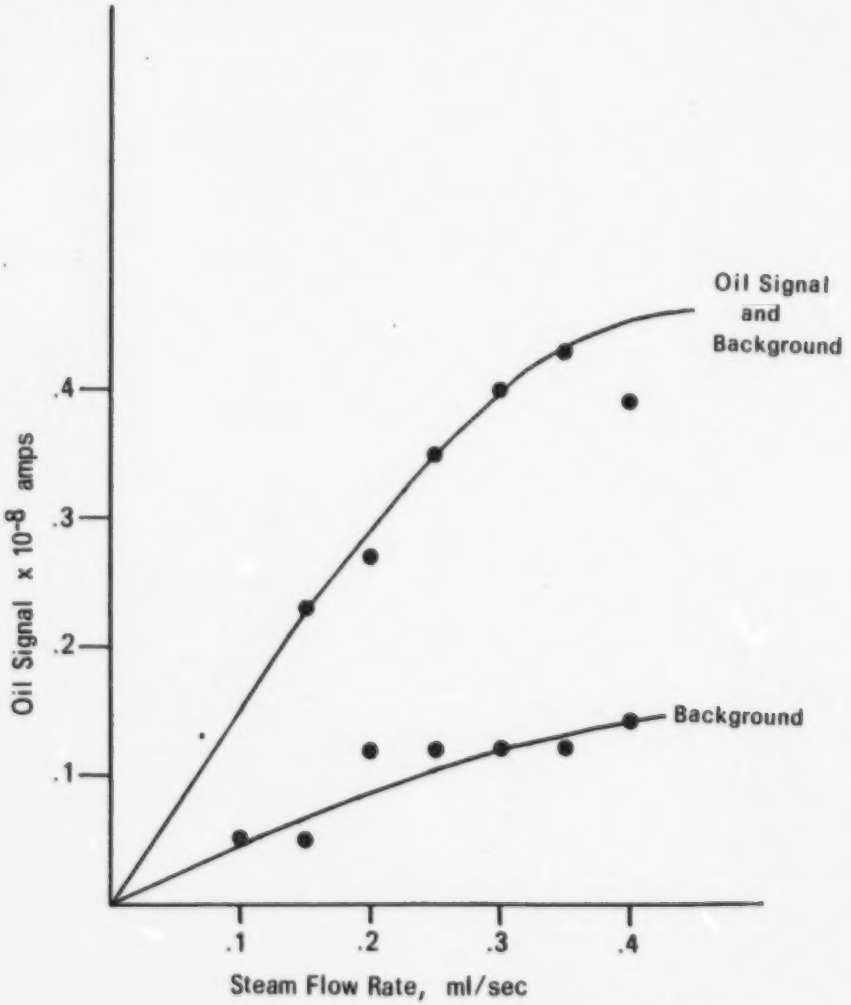


Figure 13. Effect of steam flow rate on the ability of te system to remove No. 2 fuel oil from the sample: steam temperature was 370° sample rate was 100 ml/min.

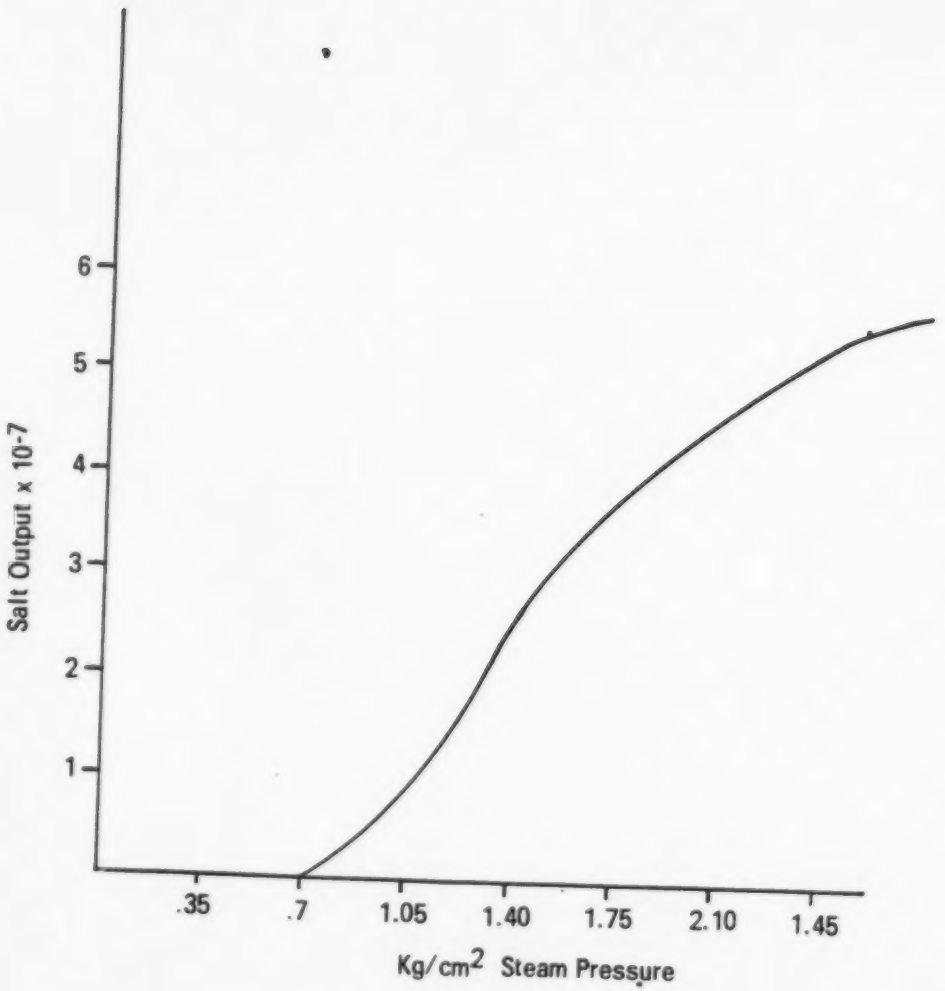


Figure 14. Output signal of 3% salt solution vs steam pressure. No baffle was used in the distillation cell, steam temperature was 370° and sample flow was 110 ml/min.

SECTION 7

DISCUSSION

The flame emission technique was evaluated as a means of detecting oil in water. The experimental method and instrumentation developed during this study was found to be sensitive to oil concentration as low as 10 ppm for oils with vapor pressures equal to or higher than No. 4 fuel oils.

The system tested during the Batch system procedure successfully detected concentrations of No. 2 and No. 4 fuel oils but the No. 6 fuel oil was not satisfactorily detected. The vapor pressure of No. 6 fuel oil was lower than No. 4 fuel oils and the steam distillation procedure incompletely removed them from the water sample. Much of the higher molecular weight compounds and asphaltenes remained in the water sample after steam distillation. Background interferences were successfully removed by steam distillation and use of a narrow band filter.

The continuous system procedure successfully detected No. 2 and No. 4 fuel oils. The instrument was less sensitive for No. 6 fuel oil. Steam flow rates were determined for the system. These are utilized for No. 2 and No. 4 fuel oil detection. Greater steam rates were employed to obtain a signal for No. 6 fuel oil. However, the system was still relatively insensitive to the No. 6 fuel oil. The physical characteristics and chemical composition of the No. 6 fuel oil made it undetectable. Interferences were removed from the system by use of a distillation cell with baffle, when steam rates less than 50 ml/min were used.

The batch system and continuous system procedure reported will detect and quantitate No. 2 and No. 4 fuel oils. Further development of the system may improve the sensitivity of the instrument to fuel oils and crude oils. It may be necessary to include a sample pre-treatment or extraction procedure to obtain maximum use of the system.

REFERENCES

1. Gaydon, A.G., 1957. The Spectroscopy of Flames, John Wiley & Sons, Inc., New York.

2. Goulden, P.D., P. Brookshank, and M.B. Day. Determination of Submicrograms Levels of Phenol in Water. Analytical Chem. 45 (14), 2430-2433, 1973.

3. Gruenfeld, M. and R. Frederick. The Ultrasonic Dispersion Source Identification and Quantitative Analysis of Petroleum Oils in Water. Rapp. P.-v. Reun. Cons. Int. Explor. Mer. 171, 33-38, 1977.

4. Robinson, J.W. and V. Smith. Emission spectra of organic liquids in hydrogen flames. Anal. Chem. Acta. 36, 489-498, 1966.

5. Veillon, C. and M. Margoshes. An evaluation of the induction-coupled, radio frequency plasma torch for atomic emission and atomic absorption spectrophotometry. Spectrochim. Acta. 23B, 503-512, 1968.

APPENDIX A

DESIGN GOALS

The U.S. Environmental Protection Agency wanted to develop an instrument that could be used to measure, on an absolute basis, the concentration of oil in oil-contaminated water. The source of the oil-contaminated water could be from on-shore oily waste disposal facilities, off-shore oil production platforms, accidental discharges of oil (tank farms, railroad tank cars, trucks, pipelines, etc.) and from similar sources and facilities where water is oil-contaminated, and where restoration and recycling of the water was to be achieved by gravity settling, or by mechanical, chemical or physical processes.

Several methods have been developed and are proposed for restoring and recycling the oil-contaminated water. Some of the methods used to separate the bulk of the oil contamination prior to discharge of the water to the environment are gravity separation, adsorption, centrifugal separation, flotation, coalescence, filtration, pressure, vacuum and other related methods.

An instrument which could measure low concentrations of oil in water (i.e., five to ten parts per million) on a continuous basis and in a reliable and economical manner was required. Oil concentration meters currently known to EPA involved the use of ultraviolet fluorescence, particulate measurement (i.e., Tyndall effect) or IR analysis. An instrument based on these techniques may or may not have the potential to measure low oil concentration in water. Although several instrument systems using methods and techniques based on electro-optical or electro-acoustical principals have been considered, no one system is presently favored over another.

Development of an instrument that could measure low concentrations of oil in oil-contaminated water was desired, according to the following basic objectives:

1. The instrument should be able to operate with minimum interference or obstruction by rust particles, pH, salinity (marine, brackish or fresh water), etc.

2. The instrument should be able to operate with a minimum amount of auxiliary equipment.

3. The instrument should be able to reject solids and debris which would interfere with the efficiency of the system or damage the instrument.

4. The instrument should be compact and readily movable from one site to another.

5. The first cost should be reasonable.

6. The operating expense should be minimal.

7. The instrument should need minimum maintenance.

8. Repairs should be able to be made easily.

9. There should be readily available replacement parts.

SPECIFIC DESIGN GOALS

The instrument was to approach the following design goals.

A. Continuously measure and record, on a real time basis, the concentration of oil in treated water discharged from either marine, brackish, or fresh water contaminated by oily waters. The limit of detection of total free, emulsified, and dissolved oil was to range from five parts per million (ppm) to 500 ppm oil concentration in water.

B. Sensitivity $\pm$ 0.5 ppm of oil (5 ppm to 10 ppm) and 10% of absolute concentration from 10 ppm to 500 ppm oil, or limit of instrument.

C. Full scale accuracy to $\pm$ 5%.

D. Digital or analog readout in ppm.

E. Automatic ranging.

F. Self calibrating.

G. Self zeroing.

H. Rugged, all-weather construction.

I. Pre-set alarm and manual alarm test button.

J. Minimum false alarm.

K. Short warm-up and stabilization.

L. Manual and automatic on/off control.

M. Self purging.

N. Self cleaning.

O. Go/no-go indicator or operating condition of instrument.

P. Power: AC 110 Hz, 5 amp maximum
DC 12 or 24 VDC, 5 amp maximum

Q. Foolproof hook-up -- no electrical damage to instrument.

R. Time required for assembly and disassembly shall be one hour or less by a person not skilled, but able to read instructions.

S. No special tools for assembly and disassembly -- prefer wing nuts and weather proof electrical hook-ups.

T. Must function normally on non-level surfaces or mountings -- up to 45° from level.

APPENDIX B

DESCRIPTION OF THE INSTRUMENTATION USED IN FLAME EMISSION SPECTROSCOPY

A typical flame photometric monitor employed in this study was shown schematically in Figure 4. Hydrogen fuel is fed into the burner at a rate of about 100 ml/min through a capillary tube and burns at the end of it. The air required for combustion and the aerosol water sample are supplied through a stainless steel tube at right angles to the capillary tube. The UV emission (431 nm) developed on combustion of the oil is measured by a photomultiplier tube. The 431 nm analytical band is isolated by a custom made narrow band interference filter with a half band width of about 10 nm and special sharp cut-off. Radiation of different wavelengths due to other substances in the water is thereby prevented from detection by the photomultiplier tube. The photomultiplier tube signal is amplified, displayed on a meter and may be recorded on a 10 mn potentiometric recorder.

The flame is ignited by a spark drawn between the capillary tube and the outer burner housing. The burner is oriented vertically with the flame pointing downward for rapid elimination of any condensed moisture. A compressor supplies air to an air aspirator connected to the burner. The sample inlet is therefore at a slightly reduced pressure allowing combustion air and aerosolized sample to pass through the burner. The aspirator is heated electrically with a cartridge heater to prevent condensation of water vapor.

There are important advantages to the use of an aspirator rather than a pump for moving air and sample through the burner. The system is always open to the atmosphere, not subject to sudden pressure fluctuations which can add to instrument noise, and there is no contamination of a pump.

It has been observed that oil sensitivity is improved by operating the burner at a relatively cool temperature (a surface temperature of about 100°C). This is achieved by blowing some of the compressor air over the outside of the burner to cool it and also by addition of nitrogen to the fuel gas.

The oil containing water is aerosolized with an ultrasonic nebulizer. Smaller, more easily vaporized droplets are obtained in this manner, and consequently, greater sensitivity. Significant improvements in response to oil have been made recently by inserting a heated tube and condenser between the nebulizer and the burner. This modification serves to condense out much of the water but not the oil, prior to introduction into the burner. There is another advantage to the ultrasonic nebulizer important in this application. The violent agitation in the nebulizer results in an intimate dispersion of the oil in the water and a more complete aerosolization. Consequently, a more accurate measurement of oil concentration can be made.

METHODS OF SAMPLING

The nebulizer can operate on only a few ml/min of sample. This small amount may be continuously fed into the nebulizer sample chamber after abstracting from the main stream of the water to be monitored. The few milliliters of sample required are quickly aerosolized, and the instrument will respond rapidly to changes in oil concentration. However, care must be taken that the sample is moved quickly to and through the monitor. This will be accomplished by abstracting the sample from the main stream at a fairly rapid rate, (approximately 100 ml/min) and passing this through tubing of small volume to the analyzer. In addition, only a small portion of this abstracted sample will be fed to the nebulizer with the larger portion being returned to the main stream. In this manner, water from the main stream reaches the detector quickly which rapidly senses changes in the composition of the water to be monitored. However, the sample abstracted must be sufficiently large to be representative of the main stream.

MAINTENANCE

During many years of development and use of flame photometric monitors, NUCOR personnel have determined that these instruments require very little maintenance. In the past, hydrogen was supplied by cylinders of fuel gas. A standard commercial No. 1A cylinder of hydrogen, at the present rate of combustion of 100 ml/min, can supply fuel for 38 days of operation. For added safety, however, it is proposed to replace the hydrogen cylinder by a solid polymer electrolyte hydrogen generator. This is desirable for safety. These require only the periodic addition of water (not electrolyte) to the generator.

In laboratory use, flame photometric monitors have required very infrequent maintenance. A glass emission tube in the burner allows the UV emission developed on combustion of the oil to be viewed by the photomultiplier tube. During many months of daily use in the laboratory, the emission tube has remained clean.

The ultrasonic nebulizer system has been used for several years by NUCOR for flame analyses of batch samples in water. No maintenance has ever been required during this time. No other significant maintenance operations have been encountered in the operation of flame photometric instruments.

FALSE ALARMS

The principal causes of false alarms would be response from interfering substances or a drift in base line. Drift is due primarily to changes in flow rates of burner temperature. Long term base line drift in NUCOR photometers are less than 3 percent and would be unlikely to result in false alarms.

CLEANING OF OPTICAL COMPONENTS

In order to maintain a fuel-rich, cool flame, the flame is shielded from the surrounding air by a short length of Pyrex tubing. The emitted radiation is transmitted by this glass tube to the interference filter and photomultiplier tube. Deposits on the wall of this tube could reduce the amount of radiation transmitted to the detector. During several years of laboratory investigation and development of flame photometers for water monitoring, such deposits have never been observed. During

operation only a few milliliters of sample water are aerosolized each minute and much of this water which may contain various impurities condenses in the preheater-condenser never reaching the burner. Combustion of the hydrogen fuel in the burner results in the formation of clean water vapor which can actually clean the glass tube. If necessary, it would be possible to clean the burner without disrupting operation by passing clean aerosolized water through it.

RESPONSE TIME

Response by flame emission spectroscopy is very rapid. Oil is detected in less than two seconds after introduction of the aerosolized sample into the burner. The preheater and condenser were inserted between the nebulizer and burner to condense much of the sample water prior to introduction into the burner improving sensitivity. The sample requires about 6 seconds to pass through the preheater and condenser. Almost 8 seconds are required for detection following nebulization. No attempts were made to modify this sample conditioning system in order to reduce response time.

The time for the sample to reach the burner depends on the lengths of the preheater and condenser (approximately 30 cm each) and the air flow rate carrying the sample aerosol to the burner. The distance between nebulizer and burner are kept as short as possible, and the sample flow rate as rapid as possible.

TEMPERATURE FLUCTUATIONS

Performance is not affected by temperature changes in the influent. Sample abstraction and nebulization are not temperature sensitive. To remove much of the water prior to detection, the ultrasonically-generated aerosol is heated and cooled condensing much of the water. Sufficient heat is applied so that even cooler than average water is vaporized in the preheater. Above average influent temperature will also have no significant effect since the cooler has sufficient capacity to remove any excessive heat.

The only temperature effect observed is that large changes in burner temperature (approximately 30°C), result in base line drift. Such great temperature changes are caused by large intentional variations in hydrogen combustion air flow or cooling air flow over the burner.

SAFETY

Flame photometric detectors are safe to operate. There are three potential hazards associated with the type of flame photometer used by NUCOR: (1) hydrogen, (2) the flame, (3) the ignitor. The flame is very tiny and is reached only by the successive removal of three separate enclosures. Ignition of the flame is accomplished by drawing a spark between the hydrogen jet and the outer housing of the burner. This is done by applying a potential difference between these burner components. The burner and the ignitor circuit are completely enclosed and are not accessible during operation of the instrument. The ignitor is actuated by means of a toggle switch and a cabinet interlock and is provided with status light location on the front panel of the instrument. Following ignition, this switch is turned off and its use is no longer required during operation of the instrument. Turning on the ignitor switch will actuate the ignitor only if the main power switch (provided also with a status light) is also

turned on.

Hydrogen from an electrolytic generator is fed directy into the burner where it is completely burned. As long as the hydrogen is combusted, it presents no hazard. A potentially dangerous situation could arise only if the flame went out and hydrogen continued to pass into the instrument without being burned. If ventilation is poor in the compartment in which the detector is kept, the hydrogen concentration could eventually increase to levels that could burn or explode if ignited. Measures should therefore be taken to assure shut-off of the hydrogen supply in case of a flame-out. A temperature sensor mounted on the exterior surface of the burner in the vicinity of the flame will rapidly sense any flame-out. When the temperature drops to a preset point (20°C) below the operating value (far beyond normal temperature fluctuation during operation) an electrically operated shut-off valve in the hydrogen flow to the burner and shut down the hydrogen generator. In this way, it is possible to cut off all flow of hydrogen within one minute of a flame-out. The instrument will be provided with an automatic re-ignition circuit to light the flame again following an accidental flame-out. NUCOR has routinely included such circuits in earlier flame detector monitors and flame-outs have rarely occurred during operation of NUCOR flame photometers.